V.E.8 Development of Alternative and Durable High Performance Cathode Supports for PEM Fuel Cells

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- · University of Delaware, Newark, DE

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Objectives

- Demonstrate a protective barrier between carbon and Pt to mitigate carbon corrosion.
- Enhance the stability of Pt particles by the bonding between Pt and the WC, oxycarbide or metal oxide substrate.
- Improve the dispersion of Pt to reduce the loading of Pt in the electrocatalysts.
- Demonstrate a possible synergistic effect because WC is catalytically active with Pt-like properties.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) Durability
- (C) Performance

Technical Targets

This project focuses on the improvement of the durability of cathode supports and catalysts in proton exchange membrane fuel cells (PEMFCs) that can meet the DOE 2015 targets for stationary and transportation applications.



Approach

Our approach includes three major collaborative efforts: 1) fundamental understanding of model systems, 2) synthesis of high surface area cathode supports, and 3) characterization and electrochemical evaluation of cathode supports. Synthesis and electrochemical evaluation of model systems will identify the surface compositions and phases that are stable under electrochemical conditions and guide the synthesis of high surface area cathode supports. High surface area powder materials will be platinized by standard methods and screened using a novel high-throughput approach. Materials showing adequate electrochemical stability and activity will be further used for extended electrode and membrane electrode assembly (MEA) evaluations.

Accomplishments

We performed the stability of WC and Pt-modified WC films using a unique system that combines ultrahigh vacuum equipment with an in situ electrochemical cell. We utilized X-ray photoelectron spectroscopy (XPS) to determine the stability of the WC and Ptmodified WC films before and after electrochemical measurements. In these measurements the WC and Pt/ WC films were exposed to sulfuric acid solutions under an electrochemical environment, either as a function of cycles in cyclic voltammetry (CV) measurements or as a function of time in chronoamperometry (CA) measurements. These films were then analyzed with XPS without exposing the samples to air. Our results indicate that the WC film is stable at oxidation potentials up to 0.8 V with respect to the normal hydrogen electrode. The deposition of submonolayer coverages of Pt further enhances the stability of WC to 1.0 V. For example, under direction methanol oxidation conditions, WC is only stable up to 0.8 V (Figure 1). Modification of WC with Pt improves stability at high potential limits (0.8-1 V, 3 minute CA exposure) likely due to the blocking of defect sites of WC by Pt (Figure 1). These

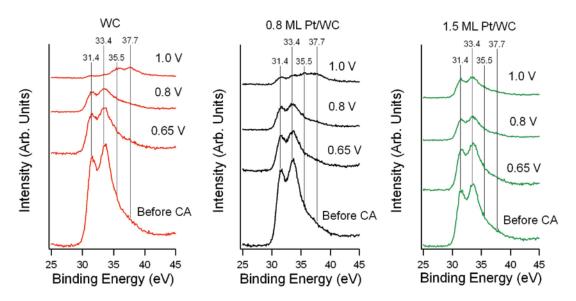


FIGURE 1. XPS after Electrochemical Evaluations

results validate the potential of using WC and Pt/WC as stable and alternative cathode materials.

We focused our synthesis effort on the development of advanced carbon supports, WC and metal oxide modified carbon surface, and synthesis of high surface area WC and conducting metal oxides. Mesoporous carbon supports have unique features for cathodes such as high surface area for Pt dispersion and large pores for oxygen diffusion. One of the key issues associated with PEMFCs is the oxidative corrosion of carbon cathodes. In FY 2007, we demonstrated that the ordered mesoporous carbon supports are more stable than the Vulcan XC-7 carbon black, and can potentially be used as a scaffold for cathode development. We also have developed a protocol to modify the surface of mesoporous carbon such that Pt particles can be uniformly dispersed on mesoporous carbon for its electrochemical testing. In FY 2007, we also developed a platinization method which allows the

deposition of Pt with uniform particle sizes (3-4 nm) on WC surfaces. This approach allows the activity and durability evaluation of various cathode supports with a minimal complication of Pt particle size variations. Using Vulcan XC-72 carbon as a scaffold, we synthesized carbon supported WC and conducting metal oxides. Preliminary results indicate that incorporation of SnO₂ improves the cathode stability, while increasing overpotential for oxygen reduction. This overpotential was reduced by modifying the method of SnO₂ incorporation. Indium oxide and TiO₂ incorporation in Vulcan XC-72 also show slight improvement, especially after exposure at 1.6 V for an hour. Platinum incorporation as nanoparticles showed enhanced activity and stability compared to platinum incorporation by incipient wetness. We demonstrated that modification with conducting metal oxides or WC provides a pathway for simultaneous improvement of electrode activity and stability.